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ALIGNED CARBON NANOTUBE TO ENHANCE THROUGH THICKNESS THERMAL CONDUCTIVITY IN ADHESIVE JOINTS (PREPRINT)

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14. ABSTRACT

Currently out of plane thermal conductivity (Kz) in adhesive joints fails to meet the needed Kz at the overall system level. Carbon nanotubes theoretically have an extremely high thermal conductivity along the longitudinal axis and according to molecular dynamics simulations the value can be as high as 3500 W/mK at room temperature for multi-walled carbon nanotubes (MWCNT). The thermal conductivity along the radial axis for MWCNTs is between 10-15 W/mK^2. Studies to increase Kz for adhesive joints only had minimal enhancement in the thermal conductivity. In order to utilize the superior thermal conductivity of the MWCNTs along the axial direction; vertically aligned MWCNTs have been used in this study. Vertically aligned MWCNTs have been grown on silicon wafers. The aligned nanotube array has been partially infused with epoxy. Selective reactive ion etching (RIE) of the epoxy revealed the nanotube tips. In order to reduce the impedance mismatch and phonon scattering at the interface, gold is thermally evaporated on the nanotube tip. A MEMS based steady state thermal conductivity measurement technique has been designed to assess the thermal conductivity of the device with special attention to the interface/transition zone.

15. SUBJECT TERMS

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TITLE: Aligned Carbon Nanotube to Enhance Through Thickness Thermal Conductivity in Adhesive Joints

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ABSTRACT

Currently out of plane thermal conductivity (K_z) in adhesive joints fails to meet the needed K_z at the overall system level. Carbon nanotubes theoretically have an extremely high thermal conductivity along the longitudinal axis and according to molecular dynamics simulations the value can be as high as 3500 W/mK at room temperature for multi walled carbon nanotubes (MWCNT)[1]. The thermal conductivity along the radial axis for MWCNTs is between 10 – 15 W/mK[2]. Studies to increase K_z for adhesive joints only had minimal enhancement in the thermal conductivity[3]. In order to utilize the superior thermal conductivity of the MWCNTs along the axial direction; vertically aligned MWNTs have been used in this study. Vertically aligned MWCNTs have been grown on silicon wafers. The aligned nanotube array has been partially infused with epoxy. Selective reactive ion etching (RIE) of the epoxy revealed the nanotube tips. In order to reduce the impedance mismatch and phonon scattering at the interface, gold is thermally evaporated on the nanotube tips. A MEMS based steady state thermal conductivity measurement technique has been designed to assess the thermal conductivity of the device with special attention to the interface/transition zone.

***Keywords**: thermal conductivity, carbon nanotubes*

The unique properties of carbon nanotubes (CNTs) have generated interest amongst many researchers over the last decade[1]. These researchers have reported remarkable electrical[2], mechanical[3], and thermal properties[4] related to their unique structure and high aspect ratio. These

unique properties make CNTs the material of choice for numerous applications like sensors[5], actuators[6], energy storage devices[7], and nanoelectronics[8].

Carbon nanotubes also have extremely high thermal conductivity in the axial direction[4] above. According to molecular dynamics simulations the value can reach as high as 6500 $Wm^{-1}K^{-1}$ at room temperature for single walled CNTs[9]. Researchers have experimentally determined the thermal conductivity of multiwalled CNTs (MWCNTs) to be 3000 $Wm^{-1}K^{-1}$ at room temperature[10]. This outstanding thermal property of nanotubes has made them target materials for thermal management materials. Thermal conductivity enhancement has also been observed in nanotube suspensions[11]. These results were theoretically intriguing as the measured thermal conductivities were abnormally greater than theoretical predictions with conventional heat conduction models[12]. Biercuk et al.[13] measured thermal transport properties of industrial epoxy loaded with as produced SWNTs (>5 wt%) from 20-300°K. It was observed that samples with 1% unpurified SWNT material showed a 125% increase in thermal conductivity at room temperature.

Unpurified carbon nanotubes were introduced to silicone elastomer to investigate their effect on the thermal conductivity[14]. Microstructure studies by a scanning electron microscope showed that the carbon nanotubes CNTs can be well dispersed in the matrix by the grinding method. The thermal conductivities of the composites were measured with the ASTM D5470 method. The thermal conductivity (K) was found to increase with the carbon amount. There was a 65% enhancement in K with 3.8 wt% CNT loading. The enhancement by equal loading of carbon black was found to be a little lower than that by the CNT loading. The composites loaded with CNTs displayed an abrupt increase in the electrical conductivity.

Thermal Interface Materials (TIM) used for dissipating heat efficiently from electronic components is gaining increased attention. Thermal conducting pads made with various conductive fillers are widely used commercially. CNTs with their exceptional thermal properties are an ideal candidate for TIM applications. Huang et al. developed TIM based on aligned carbon nanotube embedded in an elastomer[15]. Though they achieved a 120% enhancement of thermal conductivity using the nanocomposite film, the achieved value of 1.21 $Wm^{-1}K^{-1}$ was much less than the theoretical thermal conductivity of aligned carbon nanotubes. Besides TIM, the through-thickness thermal conductivity in adhesive joints is very low, limited by the low thermal conductivity of the resin used and interfacial imperfections. Thus,, in an effort to enhance the heat transfer efficiency in thermal structures, in this study we use vertically aligned carbon nanotubes to improve the through thickness thermal conductivity in adhesive joints.

[Figure 1 SEM micrograph of cross-section of as produced MWCNT Film]

Processing of the Adhesive Joint with Aligned MWCNT

MWCNT films were grown on quartz substrates by chemical vapor deposition. The aligned CNT films were prepared by pyrolyzing iron (II) phthalocyanine under Ar/H_2 at 900°C as described in details elsewhere[16]. The average diameter of the tubes was 30 nm and the average length of the MWCNT film was 30 µm. As grown, aligned nanotubes are not perfectly aligned vertically. Figure 1 shows the cross sectional view of the as produced MWCNT film. Though the vertical alignment of the nanotubes is evident from the SEM image, there are some obvious regions of imperfections, specifically bent tubes. In view of the irregularity in MWCNT alignment and imperfections, a parametric finite element analysis was performed to design the

experiment. The parametric modeling indicated that there was no effect of bent tubes on the device thermal conductivity as long as there was thermal contact between the nanotube tips and the adherent face sheet. The major results of the parametric study indicated that we needed a conductive phase to improve the thermal conductivity in the adhesive joints and we needed an interphase region which could minimize acoustic impedance mismatch between the MWCNT and adherent surface. In order to minimize the acoustic impedance mismatch between the MWCNT and adherent, the MWCNT tips were plasma etched and gold coated, whose process is discussed a little later. Prior to etching the MWCNT tips, the samples with the MWCNT side facing upwards were dipped in a beaker containing a 10% Epon 862/W - acetone solution. The film was then kept in a vacuum oven at 60°C for 2 hours for the solvent to escape. The epoxy was then cured at 177^0C for 2 hours. The epoxy-MWCNT film was then peeled off the quartz substrate by etching with a 10% HF solution. The nanotube tips were exposed selectively by etching the film surface with 32 watt RF oxygen plasma for 30 minutes. The SEM images of the film after the plasma etching are shown in Figure 2. We observe from the figure that the nanotube tips are clipped due to the plasma etching. The side of the film which was previously anchored to the substrate was similarly etched in RF plasma under abovementioned conditions. Next, a 900 nm layer of gold was thermally evaporated on both sides of the film. Pyrolytic graphite face sheets were sputter coated with Au-Pd for 3 mins. Next a thin layer of Indium metal was melt coated on the substrates and the nanotube film. Finally the nanotube film was sandwiched between the graphite face sheets and fused together by heating at 175^0C. A schematic of the assembled device is shown in Figure 3.

Figure 2 SEM micrograph of CNT film (View normal to CNT film plane)

Results and Discussions

Bulk thermal diffusivity measurements were measured using a Netzsch Laser flash apparatus under nitrogen purge. The laser flash technique allows measuring the thermal diffusivity (h) of solid materials over a temperature range -180°C to 2000°C. The laser flash (or heat pulse) technique consists of applying a short duration (< 1ms) heat pulse to one face of a parallel sided sample and monitoring the

[Figure 3. Schematic view of the assembled device]

temperature rise on the opposite face as a function of time. This temperature rise is measured with an infrared detector. A laser is used to provide the heat pulse.

The thermal diffusivity (h) measured is

$$h = \frac{\varpi}{\pi} \frac{L^2}{t_{1/2}} \tag{1}$$

where, ϖ is a constant, L is the thickness of the specimen and $t_{1/2}$ is the time for the rear surface temperature to reach half it's maximum value. Thermal conductivity can be obtained from the laser flash measurements by knowing heat capacity at constant pressure (C_p) and the density (ρ) of the specimen and is given by,

$$K = \rho C_p h \tag{2}$$

[Figure 4. Thermal conductivities of measured samples (Nanotube thermal conductivity value quoted is of the literature value**)]**

Heat capacity measurements were performed on a TA Instruments Q100 DSC. Based on the heat capacity and thermal diffusivity measurements, the thermal conductivity for the device and a graphite reference was determined at 24°C, from Eq. (2) above. The thermal conductivity values for the graphite face sheet, the epoxy and the device were measured and are presented in Figure 4. The measured thermal conductivity for the graphite face sheet, the face sheets bonded by epoxy adhesive and the actual device was found to be 400, 3 and 262 W/mK respectively. In comparison, a study of mixing nanotubes in epoxy by Huang et al.[15], as discussed above, showed considerably lower thermal conductivity (K) of 1.21 W/mK than that of our measured value. The low value of K in Huang et al.[15] work was attributed to the phonon scattering caused by acoustic impedance mismatch at the interface of the nanotube tips terminated in the epoxy (adhesive). The better thermal conductivity value of 262 W/mK in this study was achieved by our device than that of Huang et al.[15], may be due to the use of a metallic interface instead of a polymeric interface, which expectedly reduced the impedance mismatch between MWCNT and adherent surfaces. This corroborated with the results from the parametric model. The thermal conductivity of the devise (of 262 W/mK) in this study was however lower than that of the pyrolitic adherent (400 W/mK), which may be due to the use of Indium whose thermal conductivity is of ~ 70W/mK, much lower than that of pyrolitic graphite and MWCNT. Experiments are in progress using silver nanoparticles, which have a sintering temperature of ~ 150^0C. Though this device exhibited improvements in thermal conductivity, the mechanical

integrity was not addressed in this study. Micro patterned placement of the nanotube patches in adhesive joints based on thermo-mechanical modeling of the adhesive joints will be used to address this problem. A schematic of the micro patterned array is shown in Figure 5.

[Figure 5. Schematic of micro patterned placement of nanotube patches in adhesive films]

Nanotube patches would be placed in windows cut in an adhesive film. While the adhesive would provide structural strength, the strategically located nanotube patches would address to the thermal conductivity problem. Further a new test method based on steady state heat flow is being devised to measure thermal conductivity at the nanoscale of bundles of tubes. This device is also envisioned to identify the loss in conductivity at the interface.

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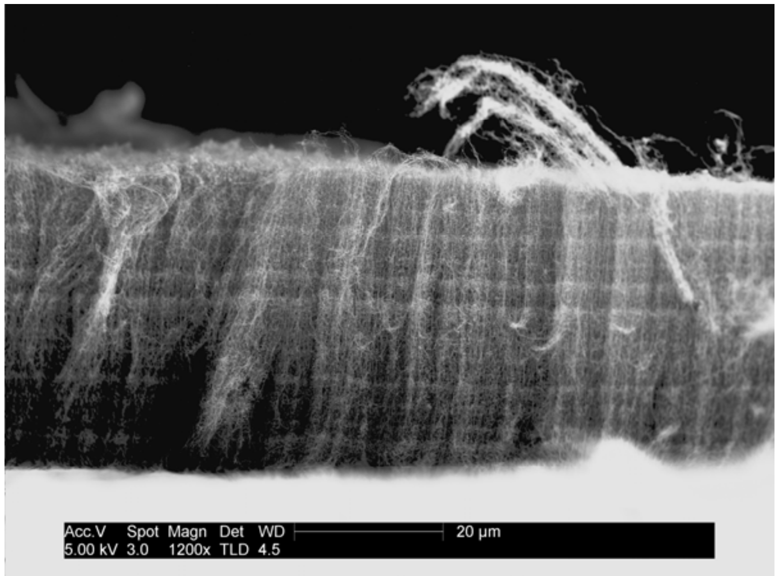

Figure 1. SEM micrograph of cross-section of as produced MWCNT Film

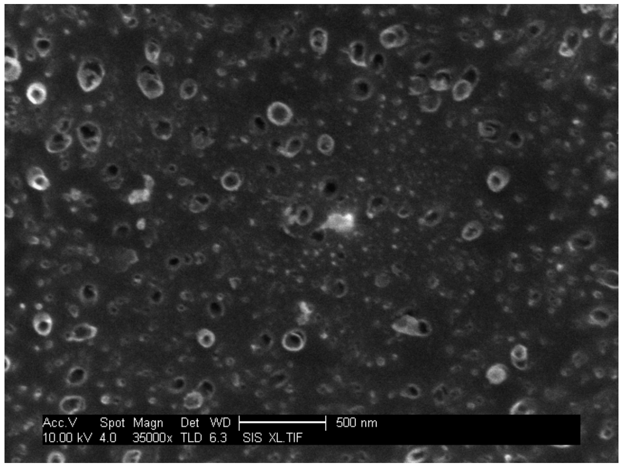

Figure 2 SEM micrograph of CNT film (View normal to CNT film plane)

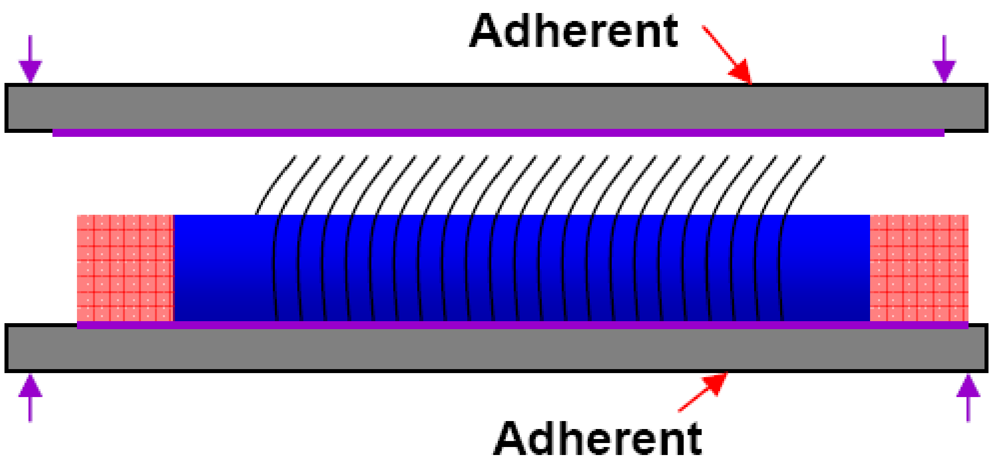

Figure 3. Schematic view of the assembled device

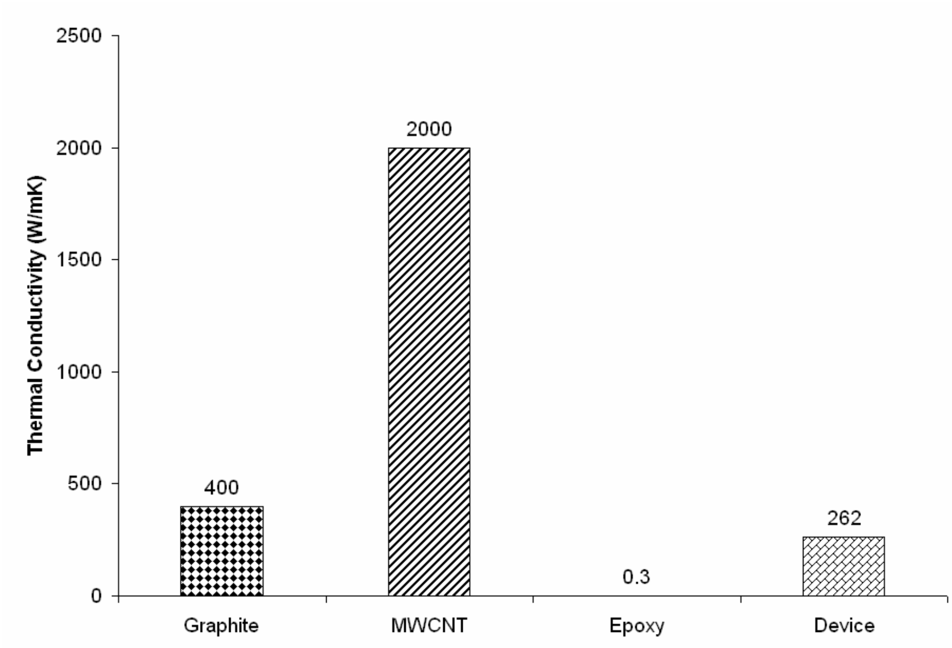

Figure 4. Thermal conductivities of measured samples (Nanotube thermal conductivity value quoted is literature value)

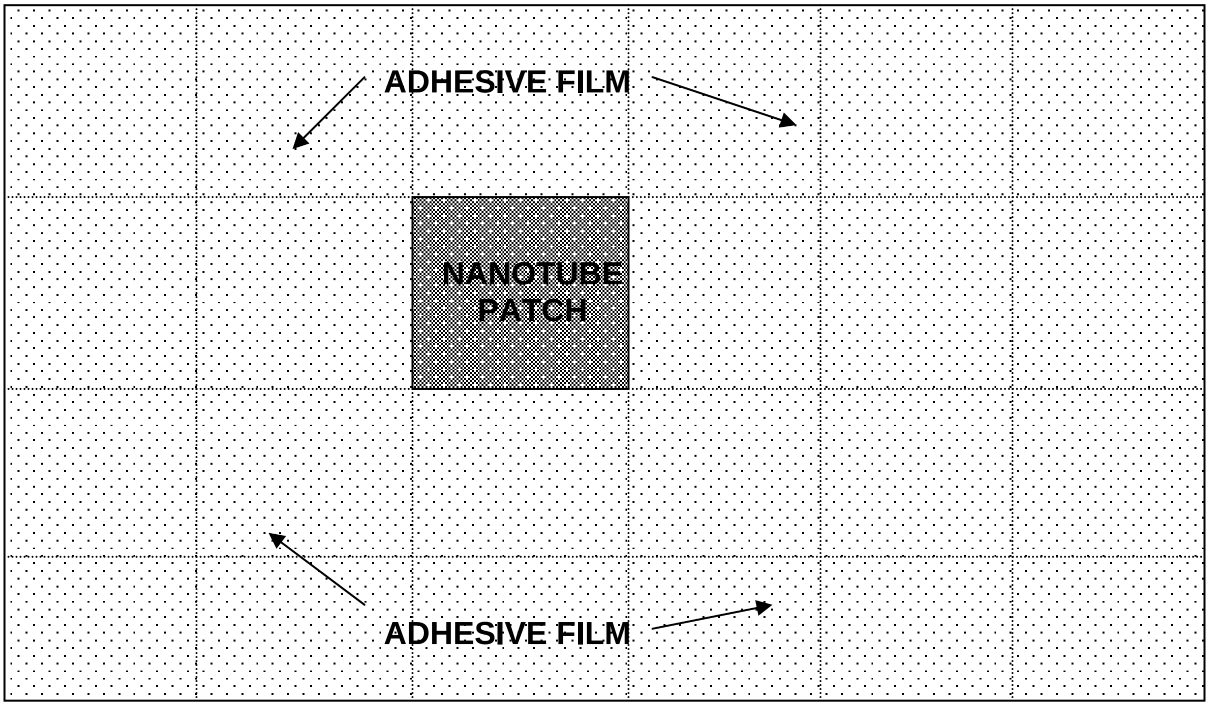

Figure 5. Schematic of micropatterned placement of nanotube patches in adhesive films